Phase equilibrium (part 2)

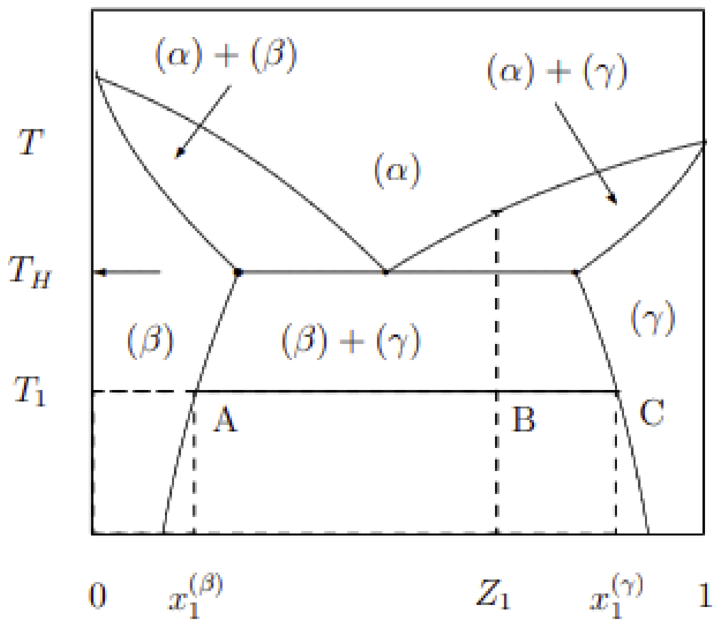
TWO–COMPONENT SYSTEMS

- When two components are present in a system c=2 and phase rule becomes in form f=4–p. In this case in addition two independent intensive variables as pressure and temperature the third factor, the composition, appears.
- A three-dimensional diagram, the description of which is quite difficult. Due to it we usually keep P or T constant and plot a two-dimensional phase diagram of two forms: pressure composition or temperature-composition dependence.

TWO–COMPONENT SYSTEMS

The phase diagram of a two-component mixture delimits the homogeneous and heterogeneous regions at different compositions of the mixture for different temperatures (isobaric diagram) or pressures (isothermal diagram)/

TWO–COMPONENT SYSTEMS



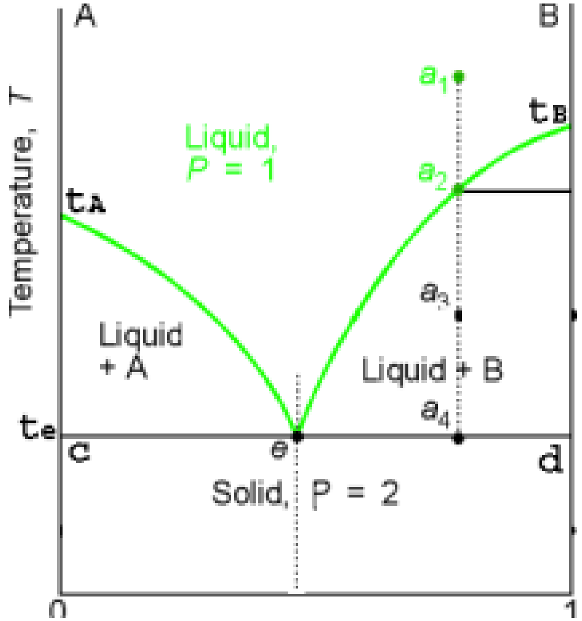
Isobaric phase diagram of a two-component system

- In the regions denoted (α), (β) and (γ), the system is homogeneous (one-phase)
- In the regions denoted (α) + (β), (α) + (γ) and (β) + (γ) , the system is heterogeneous, i.e. it is formed by two phases whose composition can be found on the binodal lines.
- The conodes (tie lines) are identical with the isotherms or isobars and they are usually not drawn

Liquid-solid phase diagram

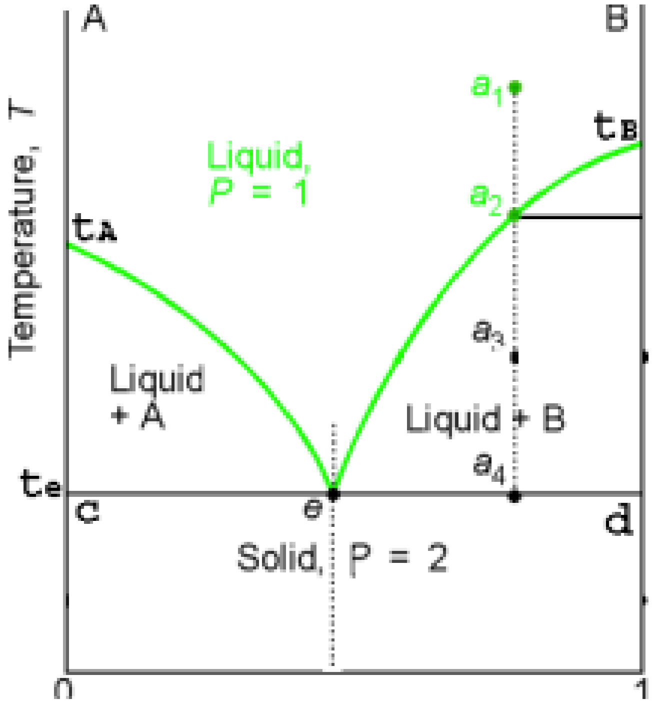
Let substances A and B are miscible in all proportions in the liquid phase and completely immiscible in the solid phase. Mixing any amounts of liquids A and B will produce a single-phase system that is a solution of A and B. Since solids A and B are completely insoluble in each other cooling a liquid mixture of A and B causes either pure A or pure B freezes out of the solution.

Liquid-solid phase diagram



- Points tA and tB are the freezing points of pure A and B (f=0). In the low-temperature limit (below the line cd) will be a two-phase mixture of pure solid A and pure solid B, since the solids are immiscible. In the high-temperature limit (above the line tAetB) we have a one-phase liquid solution of A plus B, since the liquids are miscible.
- When the point a2 reaches the solvent B begins to freeze out, giving a two-phase region with solid B in equilibrium with a solution of A and B. In this region f=2–2+1=1
- The curve tBe gives the depression of the freezing point of B and allows knowing the **freezing temperature** for each composition. At the left side of diagram the solid A begins to freeze out from the liquid mixture. This is a one-phase liquid solution of A plus B above the curve tAetB and that's why it's called the **liquidus curve** and corresponds to the temperature of the onset of crystallization for each suitable composition.

Liquid-solid phase diagram

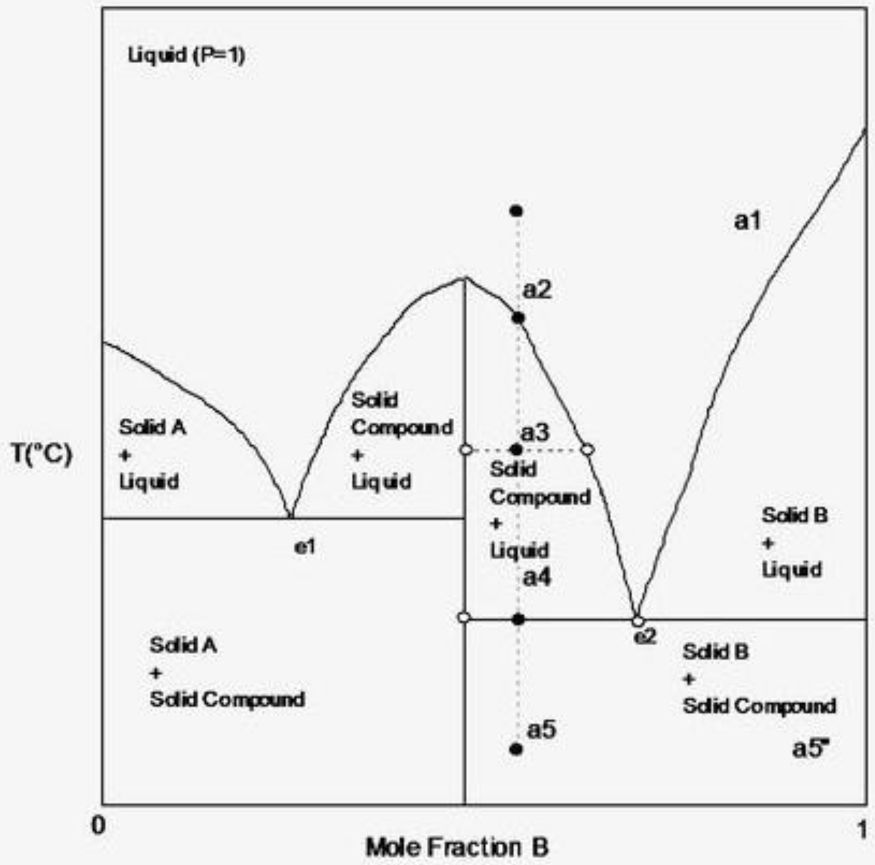


- The two freezing-point curves intersect at point e, where both A and B are frozen out together. This point is called **the eutectic point**. At point e three phases are in equilibrium – solution, solid A and solid B, so we have f=2–3+1=0.
- The composition suitable for the eutectic point is called **eutectic composition**.
- The eutectic mixture has the lowest melting point among all the rest mixtures. The temperature suitable of this point is called the **eutectic temperature** at which the temperature remains constant until all the solution has frozen and the number of phases has dropped to 2.
- Below the line cd we have a mixture of solid A and solid B and this line is called the **solidus curve**.

Liquid-solid phase diagram

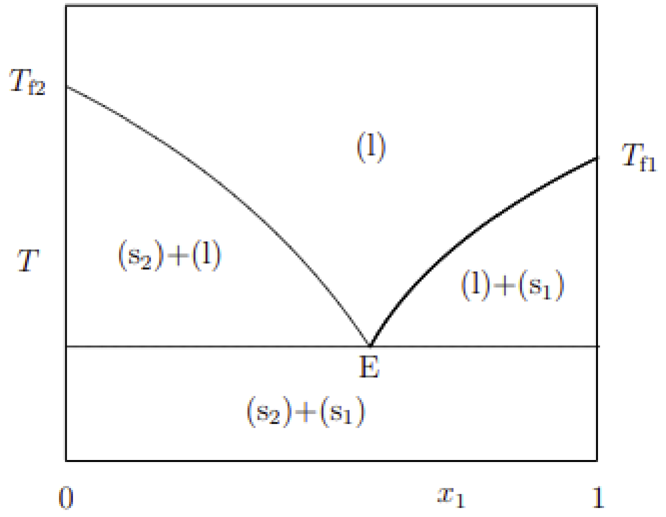
The peritectic point is the point in the vicinity of which the slopes of both curves of freezing have the same sign. At this point there are three phases in equilibrium, and according to the Gibbs phase law , the system has no degree of freedom at this point at constant pressure

Liquid-solid phase diagrams – reacting systems



- Some Binary systems react to produce one (or more) compounds
  - Definite composition
  - Unique melting point
    - Congruent melting point, I.e. melts to a liquid of identical composition
  - Maximum in phase diagram
  - Phase diagram interpreted as before except now there are additional regions

Ideal solubility

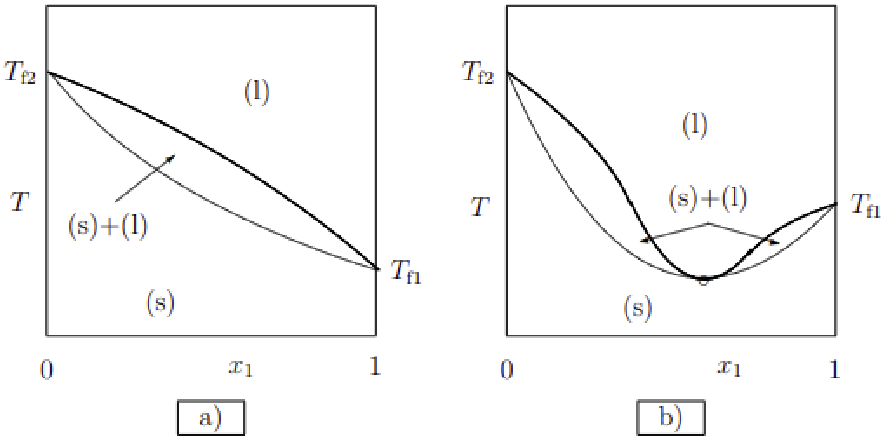


Dependence of the freezing temperature on composition in a two-component system whose components are immiscible in the solid phase. Tf,1 and Tf,2 are the freezing temperatures of pure components 1 and 2, E is the eutectic point

If the liquid phase forms an ideal solution and the enthalpy of melting is independent on temperature.

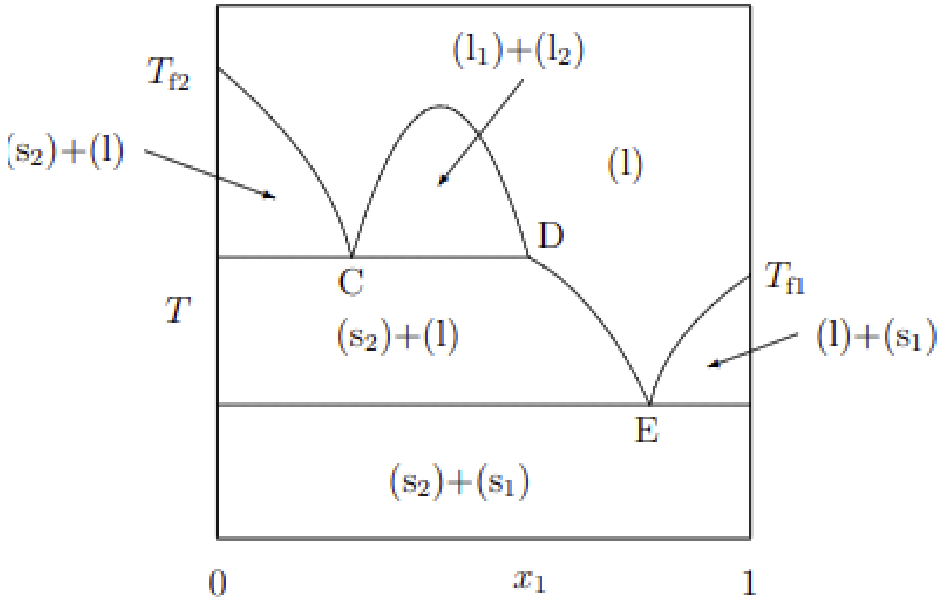
- The slope of the dependence T–x1 does not depend on substance 2.
- Solubility increases with increasing temperature.
- Of the two substances with roughly the same enthalpies of melting, the one with a lower temperature of melting will dissolve more.
- Of the two substances with a comparable temperature of melting, the one with a lower enthalpy of melting will dissolve more.

Two-component systems with completely miscible components in both the liquid and solid phases



- The liquidus is indicated by the thicker line and the solidus by the thinner line.
- Two cases of the dependence of the freezing temperature (the upper curves) and the melting temperature (the lower curves) on composition in a two-component system with components completely miscible in both the liquid and solid phases.
- Case b) is an analogy to the azeotropic behaviour.

Two-component systems with partially miscible components in either the liquid or the solid phase

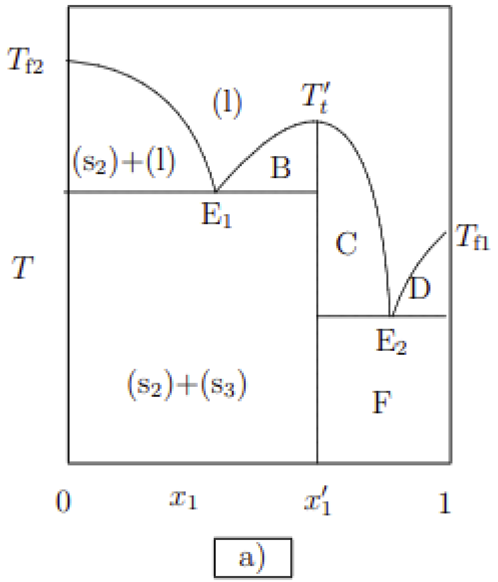


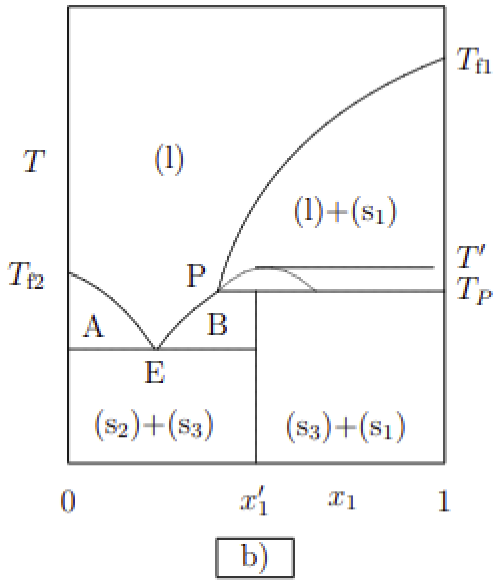
Dependence of the freezing temperature on composition for a two-component system; the liquid phases are partially miscible, the solid phases are immiscible.

Components partially miscible in the liquid phase and totally immiscible in the solid phase. Points C, D, E represent the coexistence of three phases, with the number of degrees of freedom decreasing, according to the Gibbs phase law, to zero

Formation of a compound in the solid phase

Substances 1 and 2 form a compound of composition x^0_1 . This compound is stable at its melting temperature T^0_f , which is known as the congruent melting point. The compound of composition x^0_1 is not stable at its melting temperature and T^0_f is known as the incongruent melting point in view of the fact that, in contrast to **the congruent melting point**, there is a different composition of the liquid and solid phases in this case.



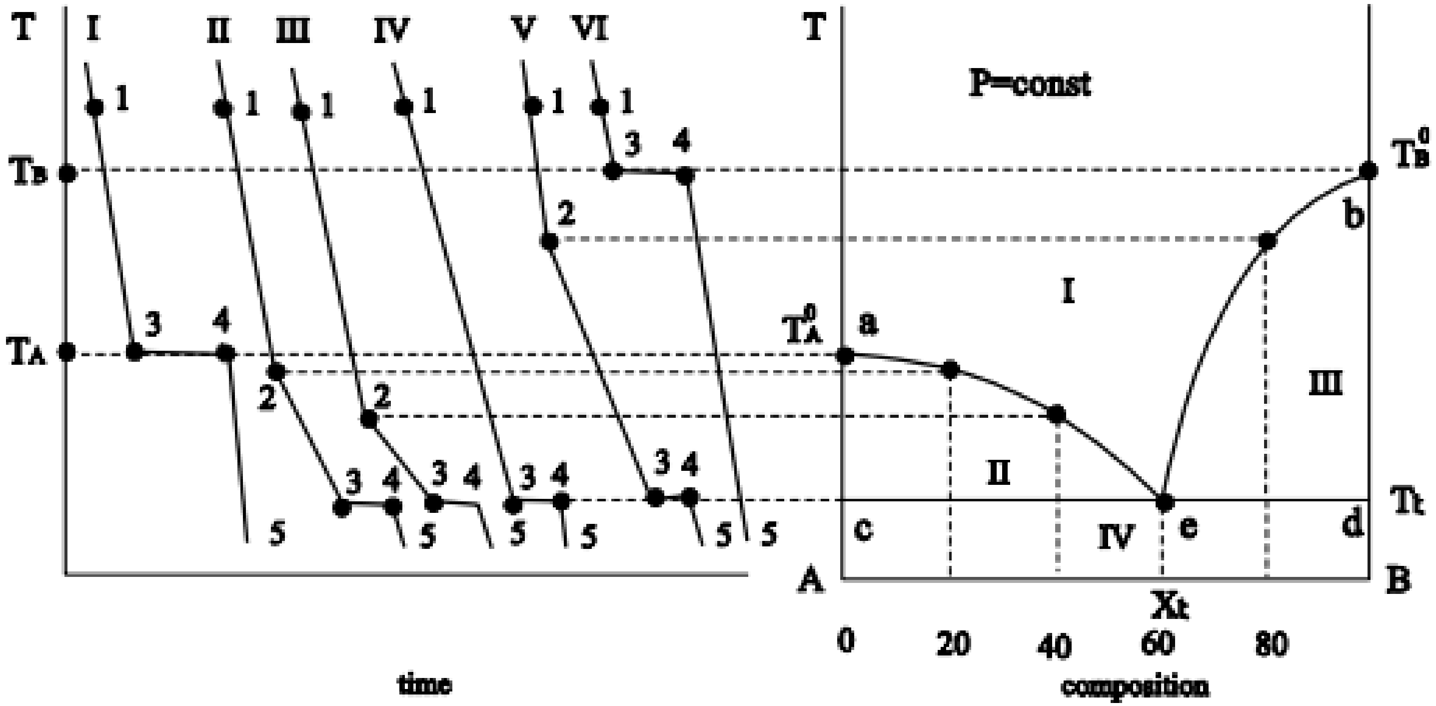


Dependence of the temperatures of freezing and melting on composition for two-component systems whose components form a compound in the solid phase. In case a) the compound is stable at the melting temperature, in case b) it is unstable at the melting temperature. Individual letters denote the following regions and points, A: (s2) + (l); B, C: (s3) + (l); D: (s1) + (l); E, E1, E2: eutectic points; P: peritectic point, F: (s1) + (s3)

Thermal analysis

One way to determine a solid-liquid phase diagram experimentally is by thermal analysis. Here, one allows a liquid solution (melt) of two components to cool and measures the systems temperature as a function of time; this is repeated for several liquid compositions to give a set of cooling curves.

Thermal analysis



Cooling curves of thermal analysis and melting diagram for system with eutectic

Thermal analysis

- The curves I and VI are for pure A and B. When pure substances are cooled, the temperature slightly falls to point 3, where the crystallization begins and the temperature remains constant while the entire sample freezes, because the heat evolved during freezing will compensate for the heat loss due to natural cooling. After the sample is frozen, further cooling causes a lowering of the temperature.
- **Cooling curves** of the pure substances exhibit horizontal sections at the melting point;
- The pure substances crystallize at certain constant temperature.

Thermal analysis

The cooling curve II. The temperature slightly falls to point 2, where the slopes of the cooling curve changes. In this point formation of crystals is accompanied by evolution of heat and causes the temperature to fall more slowly, and leads to a smaller inclination of the curves, although not to the appearance of a horizontal section. When the eutectic point is reached since both components is now crystallized from the solution, and the temperature remains constant. Further lowering of the temperature again proceeds uniformly. Melts of other compositions (curves II, III and V) exhibit similar curves with the only difference that the temperatures in the beginning of the crystallization (point 2) are different for different compositions.

Thermal analysis

Among all the compositions set apart the curve V, which freezes at constant temperature, as a pure substance (forms a horizontal section). This curve is for a liquid mixture with the eutectic composition.

The eutectic composition looks like pure substances in the following properties:

- In the eutectic point the liquid and the solid phases in equilibrium and their compositions are equal.
- The freezing temperature is unchanged.
- The number of degrees of freedom is equal to zero.

Application of thermal analyses in pharmacy

- The value of drug melting temperature gives the information about their solubility;
- The measurement of drug melting point allows to make their identification and to know the degree of purity
- Drugs having the same melting points can be identified by measurement of the eutectic temperature of the mixture of this drug with various other compounds, which, as a rule, is different

Application of thermal analyses in pharmacy

- If we know the eutectic composition of a powder or a solid drug mixture, it helps to solve the problem of drug physical compatibility.
- At the eutectic temperature, the solution crystallizes out forming a microcrystalline mixture of pure substances. This is important, if we want to obtain a tender powder for the. Microcrystalline formation increases the solubility of poorly soluble drugs that has obvious pharmaceutical possibilities.